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The discrete variational method to calculate the overlap integrals and the dipole matrix elements of the Hartree-Fock-Slater wave functions has been tested. The results indicate that the orthonormal condition for the overlap integrals is fulfilled with sufficient accuracy and that the dipole matrix elements and X-ray emission rates are in good agreement with those obtained by direct numerical integration.

KEYWORDS: Discrete Variational Method/ Hartree-Fock-Slater Wave Functions/ Dipole Matrix Element/

The discrete variational (DV) $X\alpha$ molecular orbital method[1-3] has been successfully used to study the electronic structures of the molecules. One of the great advantage of the DV-$X\alpha$ method over other molecular orbital theories is that any realistic type of basis functions and potentials, such as those numerically obtained from the Hartree-Fock-Slater model, can be used. This is because the matrix elements of Hamiltonian and overlap integrals are calculated as the weighted sums of integrand values at discrete sample points, instead of conventional numerical integration procedures.

The concept of the DV numerical integration method can also be applied for calculation of dipole matrix elements between molecular orbitals (MO) and thus for study of X-ray emission spectra.[4] As well known, there have been reported many MO methods, but it is not so easy to calculate the matrix elements by the use of molecular wave functions obtained from them because we must perform multi-center integrations. However, if we use the DV method, we can avoid the difficulties encountered in multi-center integration. It is the purpose of the present work to test the accuracy of the DV integration method for calculation of the dipole matrix elements. For this purpose, first the DV-$X\alpha$ calculations have been performed for a single free atom and then the overlap integrals and the dipole matrix elements for the wave functions obtained above have been evaluated by the DV integration method. The comparison of these results with those calculated by direct numerical integration has been made. Finally the X-ray emission rates obtained from both methods are also compared with each other.

The details of the DV-$X\alpha$ molecular orbital calculation have been described else-

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where.[3] The wave function for the λ-th molecular orbital can be expressed as a LCAO scheme

$$\phi_\lambda = \sum_i C_{i\lambda}\varphi_i, \tag{1}$$

where φ_i is the numerical basis function and $C_{i\lambda}$ is the coefficient determined variationally from the MO calculation.

Using the wave function in Eq. (1), the overlap integral S and the dipole matrix element D are written by

$$S_{\lambda\mu} = \sum_{i,j} C_{i\lambda}C^*_{j\mu}<\varphi_j|\varphi_i>, \tag{2}$$

$$D_{\lambda\mu} = \sum_{i,j} C_{i\lambda}C^*_{j\mu}<\varphi_j|r|\varphi_i>. \tag{3}$$

Here r denotes the position vector. In the DV method, the integrals in Eqs. (2) and (3) are calculated as weighted sums of the integrand values at discrete points distributed according to a certain sampling function. The choice for the distribution of sample points and determination of the integration weight for each sample point are described in detail in Ref. 5.

In the present work, the wave functions were obtained by the computer code SCAT for the self-consistent-charge DV-Xα molecular orbital method.[3] Using these wave functions, the overlap integrals and the dipole matrix elements were calculated with the modified version of the computer code SXS for the soft X-ray emission spectra.[4] The calculations were performed for single atom of Cl (Z=17) and Mn (Z=25). Throughout the present work the exchange scaling parameter $\alpha=0.7$ was used in the DV-Xα calculations. The number of sample points was taken to be $N=2000$.

Table I shows the square of overlap integrals for Cl atom. In the case of a single free atom, the molecular orbital reduces to the atomic orbital and $|S_{\mu\nu}|^2$ should be unity for $\mu=\nu$ and zero for $\mu\neq\nu$. It can be seen from the table that the square of overlap

Table I. Square of overlap integrals for Cl atom.

$\lvert<1s\rvert1s>\rvert^2$	0.99946	$\lvert<2s\rvert1s>\rvert^2$	1.85×10^{-8}
$\lvert<1s\rvert2s>\rvert^2$	2.16×10^{-8}	$\lvert<2s\rvert2s>\rvert^2$	0.99924
$\lvert<1s\rvert2p>\rvert^2$	8.66×10^{-6}	$\lvert<2s\rvert2p>\rvert^2$	1.54×10^{-5}
$\lvert<1s\rvert3s>\rvert^2$	2.39×10^{-9}	$\lvert<2s\rvert3s>\rvert^2$	6.91×10^{-8}
$\lvert<1s\rvert3p>\rvert^2$	7.11×10^{-7}	$\lvert<2s\rvert3p>\rvert^2$	7.59×10^{-7}
$\lvert<2p\rvert1s>\rvert^2$	3.86×10^{-6}	$\lvert<3s\rvert1s>\rvert^2$	2.50×10^{-9}
$\lvert<2p\rvert2s>\rvert^2$	5.24×10^{-6}	$\lvert<3s\rvert2s>\rvert^2$	6.95×10^{-8}
$\lvert<2p\rvert2p>\rvert^2$	0.99930	$\lvert<3s\rvert2p>\rvert^2$	1.08×10^{-6}
$\lvert<2p\rvert3s>\rvert^2$	3.52×10^{-7}	$\lvert<3s\rvert3s>\rvert^2$	1.00018
$\lvert<2p\rvert3p>\rvert^2$	9.03×10^{-6}	$\lvert<3s\rvert3p>\rvert^2$	3.21×10^{-6}
$\lvert<3p\rvert1s>\rvert^2$	2.34×10^{-7}		
$\lvert<3p\rvert2s>\rvert^2$	2.55×10^{-7}		
$\lvert<3p\rvert2p>\rvert^2$	9.23×10^{-6}		
$\lvert<3p\rvert3s>\rvert^2$	8.51×10^{-7}		
$\lvert<3p\rvert3p>\rvert^2$	1.00000		

Table II. Comparison of square of dipole matrix elements (a. u.) and X-ray emission rates (sec^{-1}) with those obtained by numerical integration of Herman-Skillman wave functions.

	Cl(Z=17) Dipole matrix element		Mn(Z=25) Dipole matrix element		Mn(Z=25) X-ray emission rate	
	HS[a]	DV[b]	HS	DV	HS	DV
$2p\rightarrow 1s$	4.169×10^{-3}	$4.168\times10^{3-}$	2.181×10^{-3}	2.197×10^{-3}	4.362×10^{14}	4.396×10^{14}
$2p\rightarrow 2s$	1.750×10^{-1}	1.752×10^{-1}	6.637×10^{-2}	6.615×10^{-2}	7.737×10^{10}	7.699×10^{10}
$3s\rightarrow 2p$	1.316×10^{-2}	1.328×10^{-2}	3.681×10^{-3}	3.687×10^{-3}	2.110×10^{11}	2.121×10^{11}
$3p\rightarrow 1s$	2.366×10^{-4}	2.506×10^{-4}	1.938×10^{-4}	1.946×10^{-4}	5.164×10^{13}	5.188×10^{13}
$3p\rightarrow 2s$	1.101×10^{-2}	1.169×10^{-2}	8.701×10^{-3}	8.684×10^{-3}	2.876×10^{12}	2.879×10^{12}

[a] Direct numerical integration with Herman-Skillman wave functions (Ref. 7).
[b] Discrete variational method.

integral is unity with accuracy better than 10^{-3} and becomes zero within accuracy of 10^{-5}. These facts mean that the orthonormal condition for the atomic wave functions is well reproduced by the use of the DV integration method and indicate the validity of this integration method for calculation of matrix elements.

In the Xα method, it is usual to calculate the dipole matrix element for electron transition using the Slater's *transition-state* concept,[6] *i. e.* the electron concerned with the transition stays half in the initial state and half in the final state. However, for simplicity we used the *frozen-orbital* approximation and the calculations for the dipole matrix elements were made for the ground-state configuration. The numerical results for the square of the dipole matrix elements for Cl and Mn atoms are expressed in atomic units and listed in Table II. In order to compare with the present results, the nonrelativistic atomic Hartree-Fock-Slater calculations were carried out with the computer code of Herman and Skillman (HS)[7] and the dipole matrix elements were evaluated by direct numerical integration. The obtained values are also listed in Table II. It should be noted that the exchange scaling parameter in the original HS code was set to be $\alpha=1.0$. Since this choice of α yields larger dipole matrix elements than those for $\alpha=0.7$, the numerical values in Table II were evaluated with $\alpha=0.7$. From Table II, it is seen that all the values of the dipole matrix elements, except for $3p\rightarrow 1s$ and $3p\rightarrow 2s$ transitions in Cl, are in good agreement with each other within 1%. For two transitions involving $3p$ shell in Cl atom, the DV values are about 6% larger than the HS values. This can be ascribed to the fact that in the HS code the Latter tail correction[8] is applied for the atomic potential. This correction affects on the energy and wave function of the outer-shell electrons. In Cl atom, the $3p$ shell is the outermost shell and the wave function for this shell is considerably modified by the Latter correction. On the other hand, in Mn atom there are $3d$- and $4s$-shell electrons outside the $3p$ shell and the agreement between the present results and the HS values is very good.

The X-ray emission rates in sec^{-1} is given by[9]

$$T=8.0\times10^{9}\frac{N_i}{3}\frac{\max(l_i,l_f)}{2l_i+1}E_X^3D^2, \qquad (4)$$

where N_i is the number of electrons in the initial shell, E_X is the X-ray energy in the

rydberg, D is the dipole matrix element in atomic units, and l_i and l_f are the orbital quantum numbers of the initial and final shells.

In Table II, the X-ray emission rates for Mn atom calculated by the DV method are compared with those obtained by direct numerical integration of the HS wave functions. The X-ray transition energies were estimated from the difference between the energy eigenvalues of the orbitals concerned. It is clear from the table that agreement between the DV and HS values is better than 1%.

In conclusion, the DV integration method gives the orthonormal condition for the atomic wave functions with sufficient accuracy and the dipole matrix elements and the X-ray emisson rates calculated by this method are in agreement with those obtained by direct numerical integration, within 1%. Considering the difference in the numerical procedures to calculate the wave functions between the DV-Xα program and the HS code, the accuracy of the DV integration method would be much better.

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